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ESTIMATION OF THE HOMOGENIZATION TEMPERATURE

OF A 1,2 POLYBUTADIENE/1,4 POLYBUTADIENE DIBLOCK COPOLYMER

USING RHEOLOGICAL TESTING METHODS

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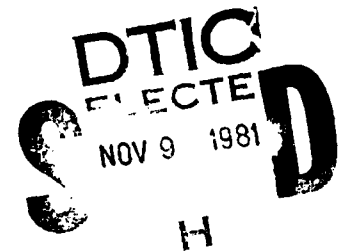| REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Four samples containing various proportions of 1,2 and 1,4 polybutadiene were subjected to a series of rheological tests in which the dynamic storage modulus was determined over a range of temperature (30°C-160°C) and frequency (0.1-100 rad/sec). Isochronal plots of G' vs temperature showed that one of the samples (diblock 30/50, containing 38% 1,2 polybutadiene) was substantially different in its rheological behavior. Appropriate treatment of the data revealed a "rubberlike" plateau at low frequencies which began to disappear around 70°C and was completely missing at 100°C and above. From these results it was

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tentatively concluded that this sample undergoes a transition from a hetero-
geneous to a homogeneous morphology between 70° C and 100° C.

INTRODUCTION

In previous reports and publications from this laboratory we have dis-
cussed various aspects of rubbery/rubbery diblock copolymers and polymer
blends. Particular emphasis has been placed on morphology and mechanical
behavior, and interrelations between them. Considerable attention has been
given recently to a rubbery/rubbery system comprised of 1,2 polybutadiene
and 1,4 polybutadiene. At room temperature, blends of homopolymers of 1,2
polybutadiene and 1,4 polybutadiene were found to be heterogeneous in
essentially all proportions and molecular weights (M>14000). On the other
hand, under similar conditions diblock copolymers of the same materials
(1,2B/1,4B) were either homogeneous or heterogeneous, depending on molecular
weight and composition (1). All of these observations were explained recently
(2) in a self-consistent manner using existing thermodynamic theories for
phase separation in block copolymers and polymer blends (3,4).

One of the interesting unanswered questions remaining from the previous
work mentioned above is whether or not an increase in temperature would
lead to a transformation from heterogeneous to homogeneous materials as
predicted by the theories (3,4). Particularly interesting among the
materials studied is the 1,2/1,4 diblock copolymer designated 30/50 [a di-
block copolymer comprised of 30,000 molecular weight sequence of 1,2
polybutadiene followed by a 50,000 molecular weight sequence of 1,4 poly-
butadiene] because its coordinates on the generalized room-temperature
"phase diagram" (2) placed it very near the boundary separating homogeneous
and heterogeneous diblock copolymers. Thus a moderate increase above room
temperature might be expected to lead to the expected transition.

Of the various methods for examining heterogeneous-to-homogeneous transitions in block copolymers, small angle x-ray or neutron (employing partially deuterated block copolymers) scattering methods are probably the most versatile and reliable. For the 1,2B/1,4B system under consideration here, only neutron scattering experiments on specially prepared deuterated samples would be expected to work since the electron density difference required for x-ray work would be very small. We felt, however, that it would be useful to attempt to make a first rough estimate of the afore-mentioned transition temperature for our existing protonated samples by carrying out certain rheological tests using the method of Gouinlock and Porter (5). Our purpose is to verify the existence of the transition and to locate the regime of temperature over which it occurs. This rheological method has been employed successfully in our earlier work on blends of 1,4 polybutadiene and cis 1,4 polyisoprene (6).

MATERIALS

Four samples (Table 1) were subjected to rheological testing. One of these, sample 30/50 (a heterogeneous diblock) was the material of central interest for reasons discussed above. Sample 30/100, shown earlier to be a homogeneous diblock copolymer, was included in the study for purposes of comparison. Also two homopolymers 1,2B and 1,4B were included because these are known to be well-behaved, "thermorheologically simple" (7) materials in rheological tests of the type used here

TABLE 1

Characteristics of Polymers Tested

Sample Code	$\overline{M}_n$(1,2 Block)	$\overline{M}_n$(1,4 Block)	Weight Fraction 1,2B	$\overline{M}_{n,t}$(25°C)[*]
30/50	32000	52000	0.38	85000
30/100	31000	102000	0.23	136000
90/0	90000	0	1.00	∞
0/100	0	100000	0	∞

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[*]$\overline{M}_{n,t}$ signifies the number average molecular weight at the transition from homogeneous to heterogeneous regions of a generalized phase diagram (2). Above $\overline{M}_{n,t}$ diblock copolymers are expected to be heterogeneous; below $\overline{M}_{n,t}$ they are homogeneous. Values of $\overline{M}_{n,t}$ for diblock copolymers of various compositions of 1,2B/1,4B are calculated (8) using Helfand's computer program (3) which describes phase separation in block copolymers. Necessary input parameters involving AB interactions are estimated (8) using solubility parameters from the literature (9).

Films of the various polymers were obtained by spin-casting from cyclohexane solutions. All specimens contained 0.2 weight percent of an antioxidant, Antiox 330 (Ethyl Corporation). Films (about 0.5 mm thick) were vacuum dried and stored in the dark at -5° C.

RHEOLOGICAL METHODS

Several years ago Gouinlock and Porter (5) examined the rheological behavior of a low molecular weight SBS triblock copolymer over a wide range of temperature. In isochronal plots of dynamic modulus against

temperature, they observed a "discontinuity" which was most pronounced in the low frequency data (5). They interpreted their results as evidence of a "phase transition" from a heterogeneous to a homogeneous material. The temperature of the rheological discontinuity was in good agreement with other observations of and predicted values of the homogenization temperature for polystyrene/polybutadiene block copolymers (5), thus enhancing the credibility of their interpretation.

We have carried out similar experiments using a Rheometric Mechanical Spectrometer in the eccentric rotating disc mode. Temperature of the experiments varied from 30 to 160° C and the frequency range was 0.1 to 100 rad/second. Two sets of platens were used, having diameters of 2.5 cm and 7.2 cm respectively. Considerable effort was expended to ensure that crosslinking did not occur to any appreciable extent during the rheological tests (10). Various corrections for apparatus thermal expansion and apparatus compliance were applied as needed (10). Test specimens consisted of a 3-layer stack of samples squeezed down into a 1 mm gap in the Rheometrics instrument and trimmed to final dimensions. Shear strain amplitudes were always less than 0.25 and it was observed that linear viscoelastic response was obtained in this region of strain. Table 2 summarizes the experimental program for each of the four samples studied

TABLE 2

Sample Code	(90/0)	(30/50)*	(30/100)	(0/100)
Diameter (cm) Disc	2.5	(a) 2.5 (b) 2.5 (c) 7.2	2.5	2.5
Frequency range (rad/sec)	0.1-100.0	(a) 0.1-1000 (b) 0.1-100.0 (c) 0.1-10.0	0.1-100.0	0.1-100.0
Temperature range (°C)	30-150	(a) 35-150 (b) 30-90 (c) 70-160	30-130	30-122
Temperature interval between measurements	20	(a) 25 (b) 10 (c) 10	20	30

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*3 separate experimental runs were performed on sample 30/50

RESULTS

Figures 1-5 show plots for each sample of the logarithm of the storage modulus, G', against temperature for various fixed frequencies. Similar plots were constructed for the loss modulus, G", but no extra information on the transition phenomenon under consideration here could be obtained from these data and thus they are not shown here. As expected for all these uncrosslinked polymers, G' is a monotonic nonincreasing function of temperature. For samples 90/0, 30/100 and 0/100 the decrease in G' over the entire temperature range is smooth and continuous. In Figures 3 and 4, representing the behavior of sample 30/50, there are extra features in the G' vs temperature curves. These are particularly apparent in the low frequency data.

DISCUSSION

From Figures 1-5, it is possible to see at a glance that sample 30/50 exhibits rheological behavior which is qualitatively different from that of the other three samples. As mentioned above, from previous work we expect sample 30/50 to be a heterogeneous material at room temperature whereas the other three samples are homogeneous. Thus it is reasonable to attribute the observed differences in rheology to the two-phase structure of 30/50. The main question, however, is whether or not the features of the curves in the region of 70-100°C can be associated with the homogenization transition mentioned in the introduction. The change in slope seen in this region, particularly in the low frequency data, is not unlike that seen in the data of Gouinlock and Porter (5) and of Cohen and Ramos (6) where a transition from homogeneous materials was suggested.

To test further the hypothesis that homogenization of sample 30/50 occurs in the region of 70-100°C we constructed rheological "master curves" (11). This was accomplished by crossplotting the data of Figures 1-5 to obtain isotherms (log G' vs log ω) and by subsequent shifting of these curves along the frequency axis to obtain superposition. Figure 6 shows the shift factors required to carry out this frequency-temperature reduction (11) procedure for each material. For samples 90/0, 30/100 and 0/100 essentially perfect superposition was obtained over the entire range of temperature and frequency. In two separate data sets, however, the master curve for sample 30/50 showed two branches, one for data obtained below about 100° C and another for data above 100° C. This is again quite similar to the rheological behavior of SBS block copolymers in the region of the homogenization transition (5). Referring to Figure 8, below 100°C the

the 30/50 material shows a tendency to develop a low frequency "rubber-like" plateau in the storage modulus, attributable to the structured, two-phase morphology. Above 100° C this tendency is lost and the storage modulus drops off rapidly in a "liquid-like" fashion similar to that shown by the three other homogeneous materials examined here. In Figure 9 where there are more dense data points in this region of temperature and frequency, it appears that there is a continuous breakdown of structure which begins near 70° C and is complete near 100° C. Thus we can infer from these rheological measurements that the homogenization of sample 30/50 takes place over the temperature range 70° C to 100° C.

CONCLUSIONS

It is clear that sample 30/50 exhibits different rheological charac-teristics than samples 30/100, 90/0 and 0/100; these differences are most pronounced in the region of temperature between 70° C and 100° C and they show up most clearly in low frequency measurements. By crossplotting the data and subjecting each data set to a frequency-temperature reduction scheme, it became clear that sample 30/50 showed some extra "rubberlike behavior" near 70° C which gradually diminished with increasing temperature and completely disappeared by 100° C. In the face of this evidence and in comparison with earlier work (5), we tentatively conclude that homogeni-zation of sample 30/50 begins at 70° C and is complete near 100° C. Clearly rheological tests of this sort provide only a crude and indirect measure of this interesting and important phenomenon. More direct and clear determinations of the homogenization transition should be possible using ot: methc , particularly various radiation scattering experiments.

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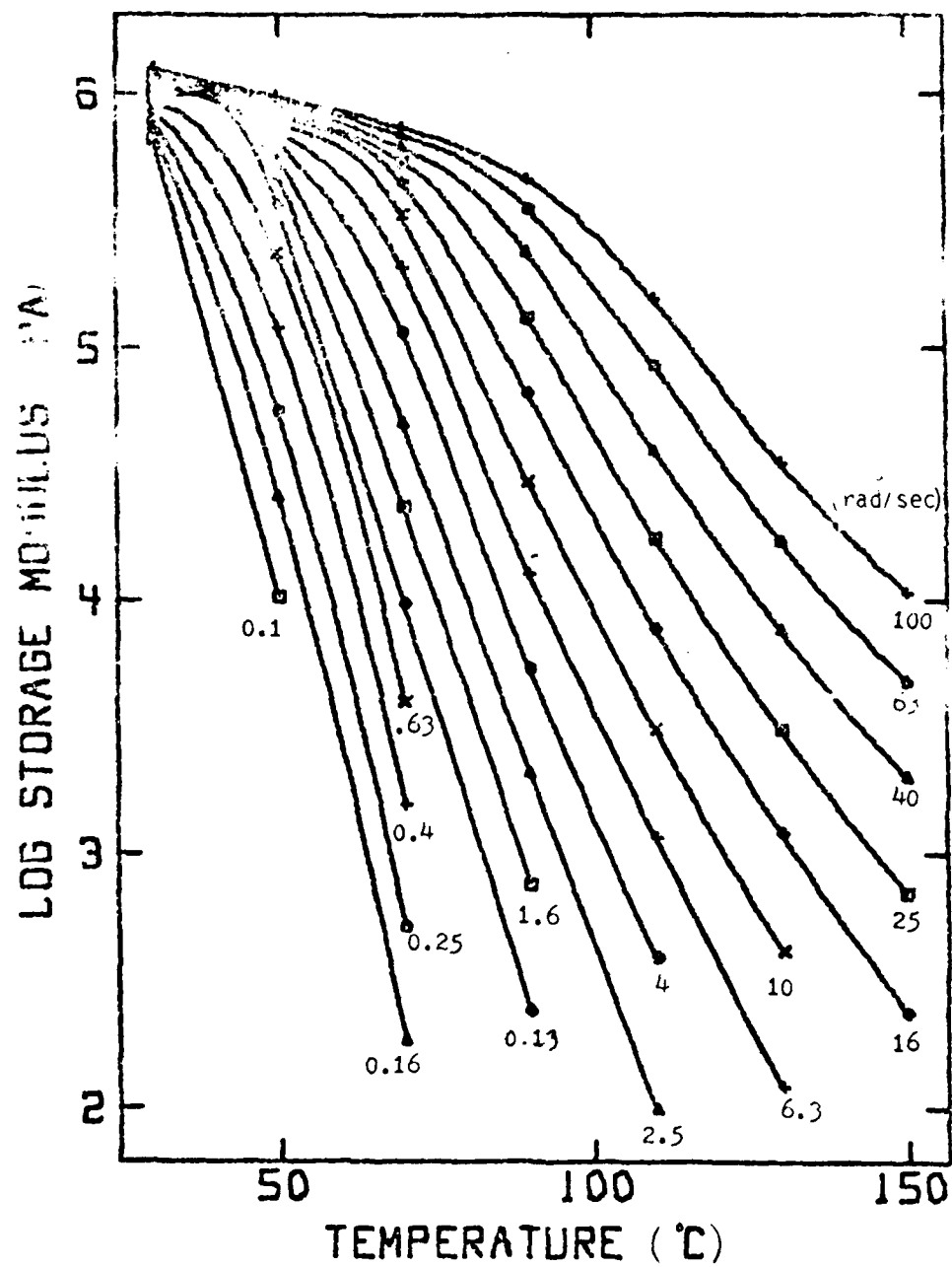
Figure 1. Isochronal (values of frequency in rad/sec shown next to each curve) plots of log G' vs. temperature for sample 90/0.
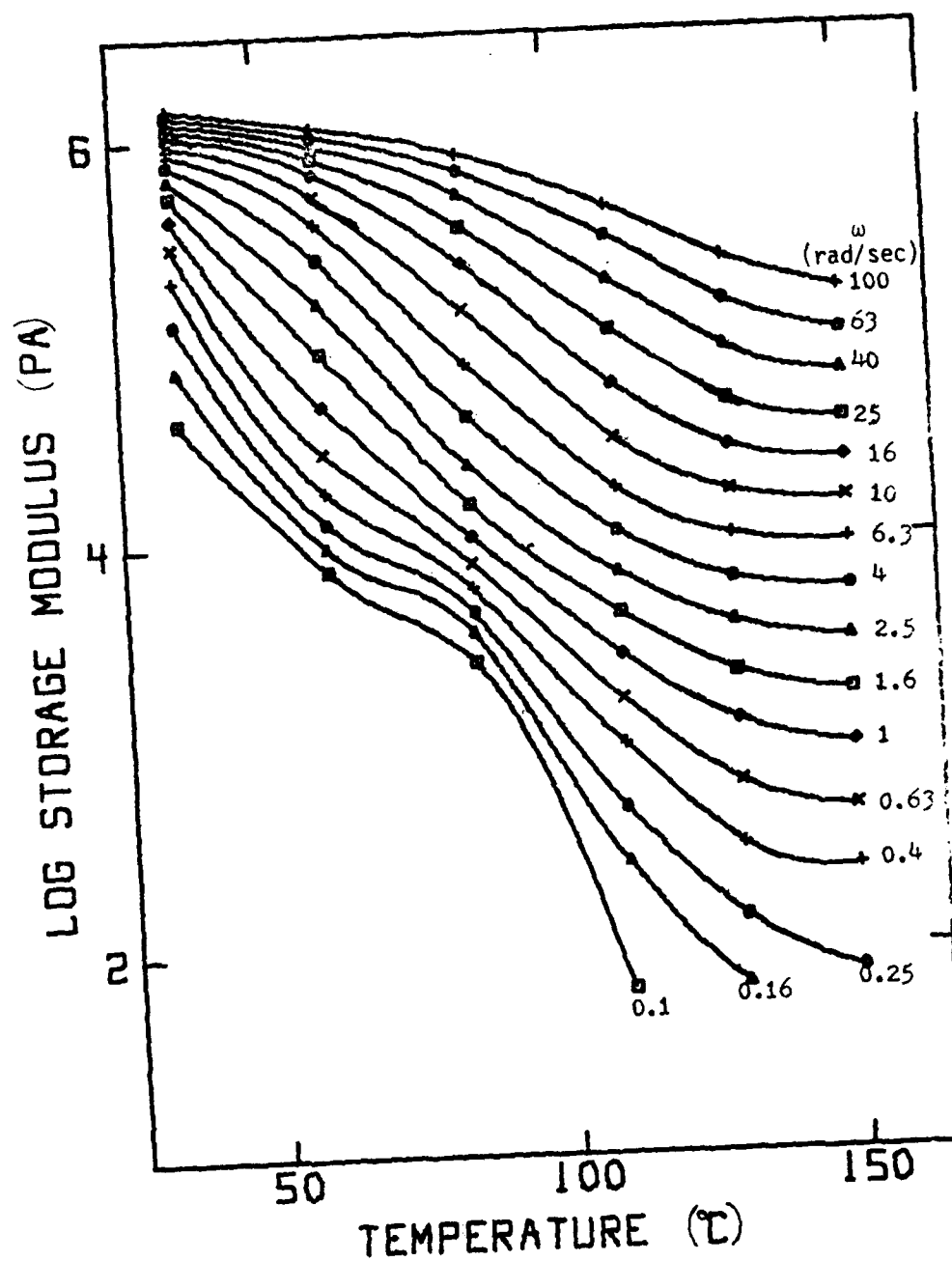
Figure 2.   Isochronal plots of log G' vs. temperature for sample 30/50 (run a).
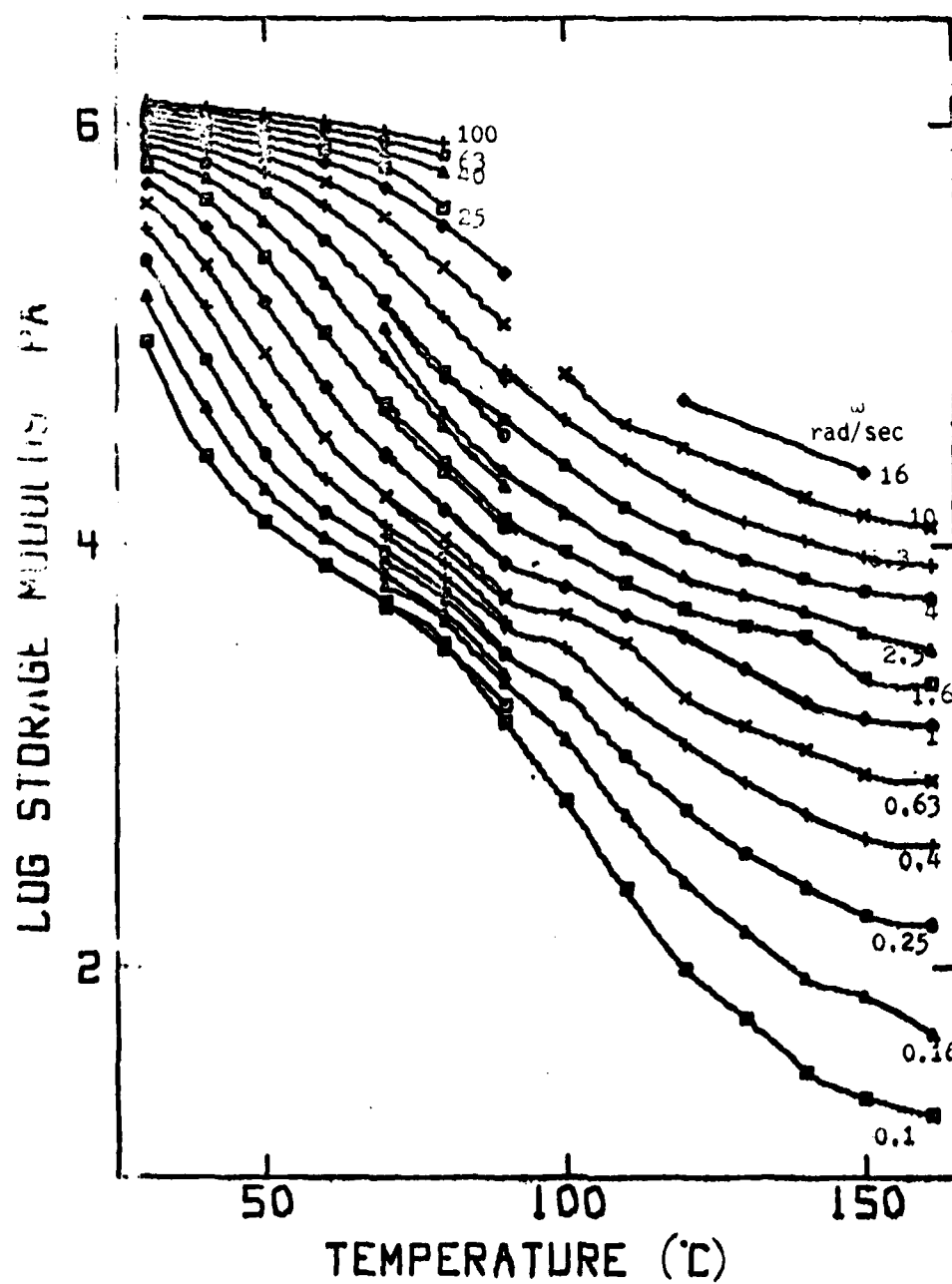
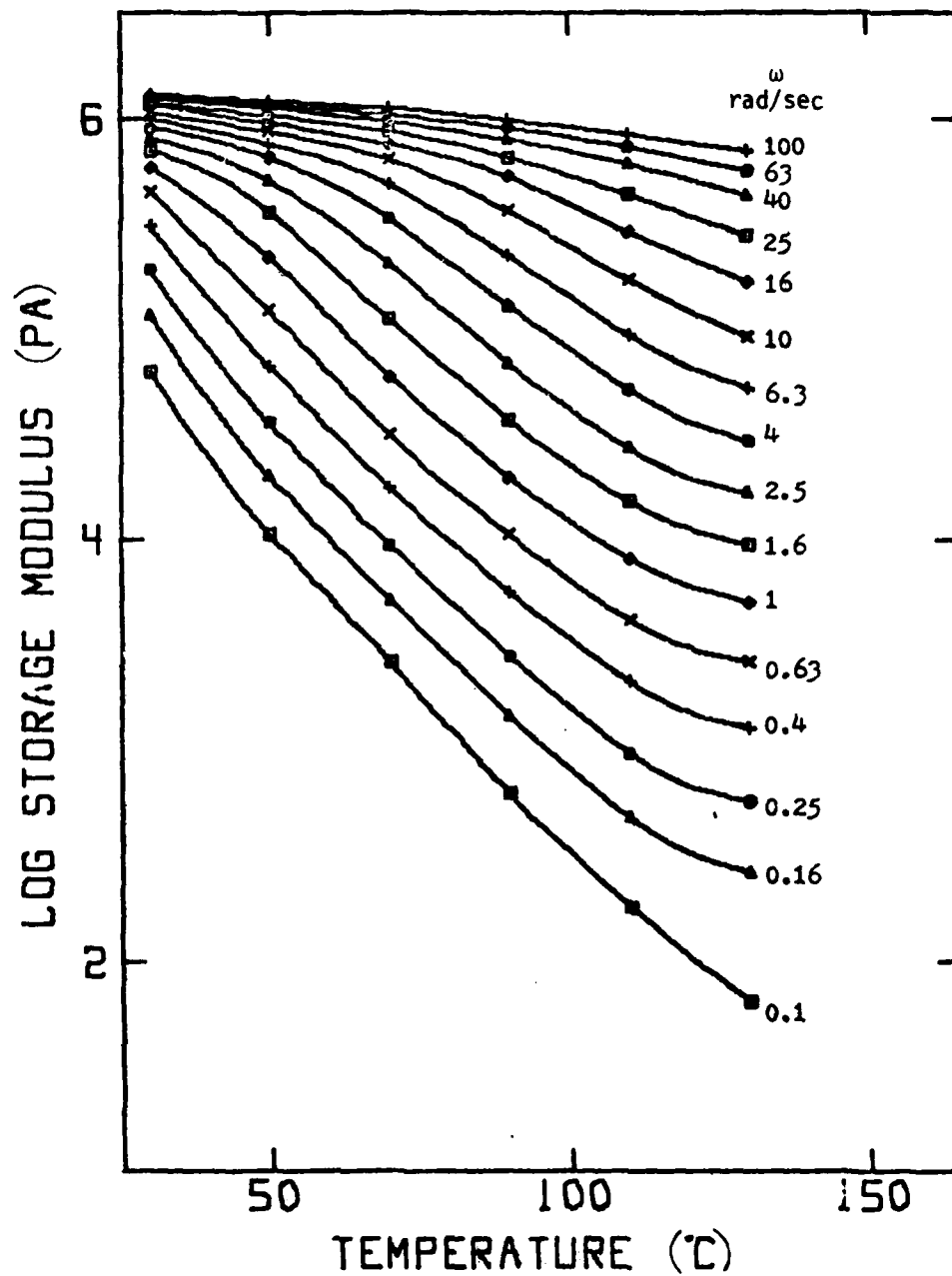Figure 3. Isochronal plots of log G' vs. temperature for sample 30/50 (runs b,c).

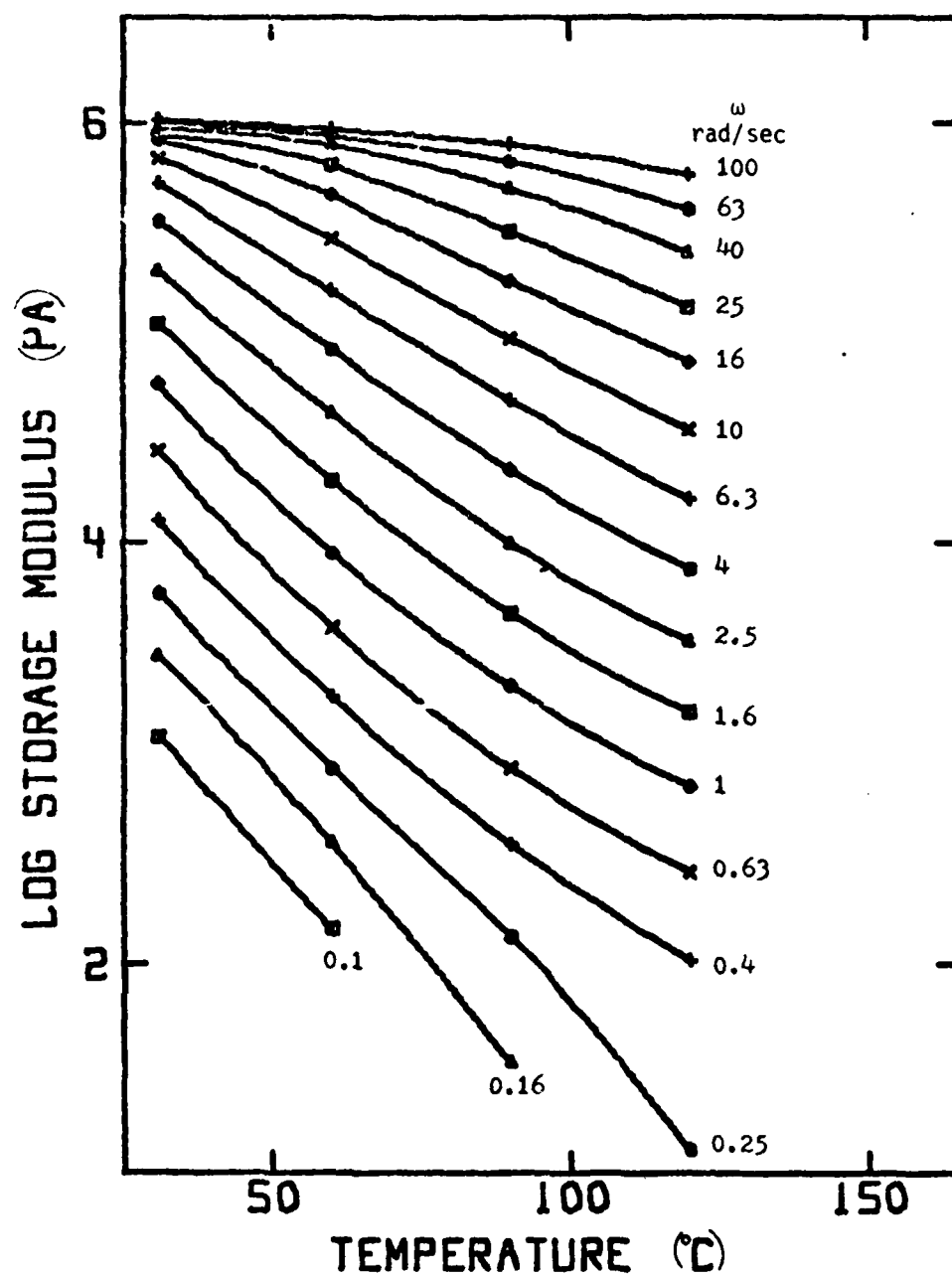Figure 4. Isochronal plots of log G' vs. temperature for sample 30/100.

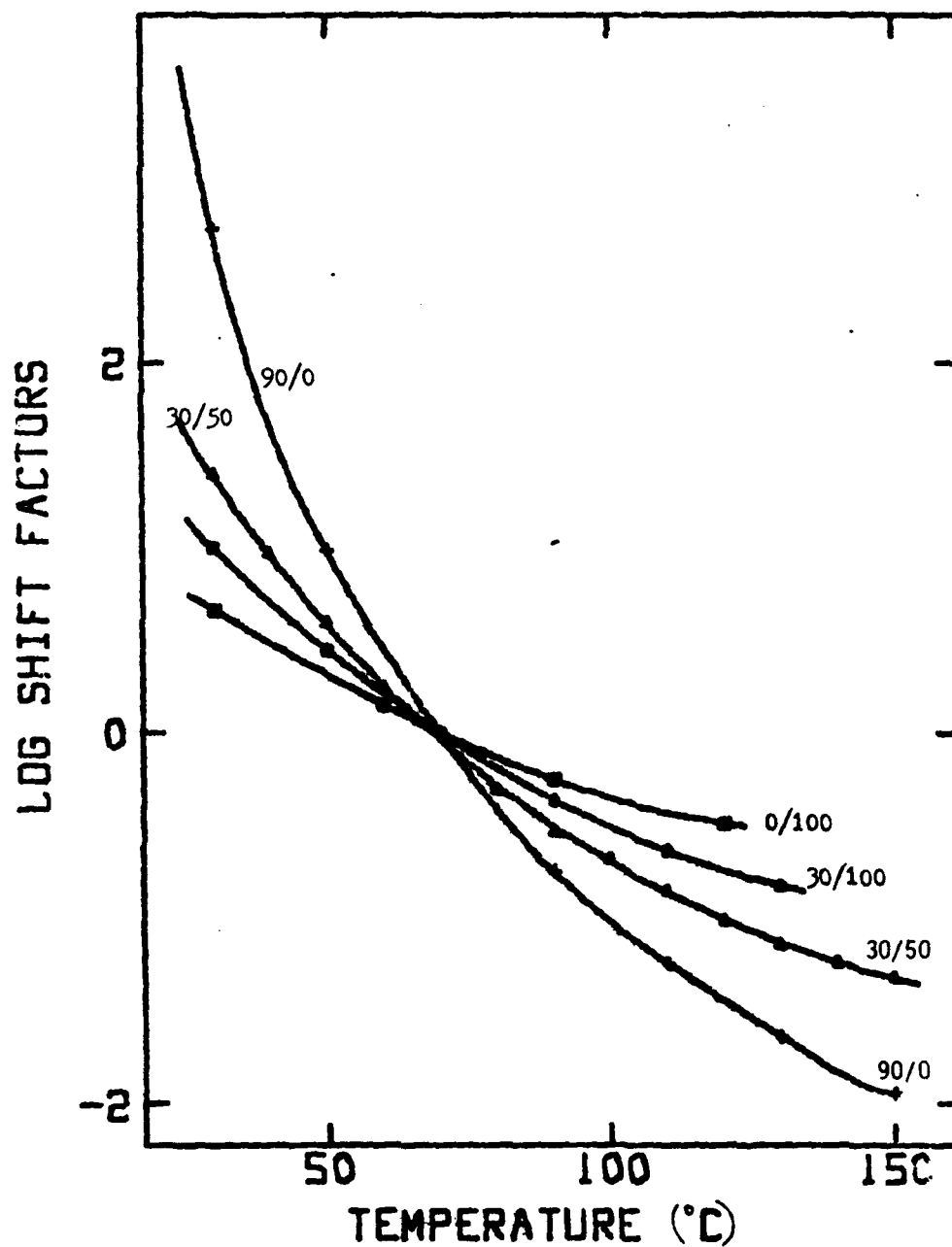Figure 5. Isochronal plots of log G' vs. temperature for sample 0/100.

Figure 6.   Shift factors for the various polymer samples.
reference temperature = 70 °C.
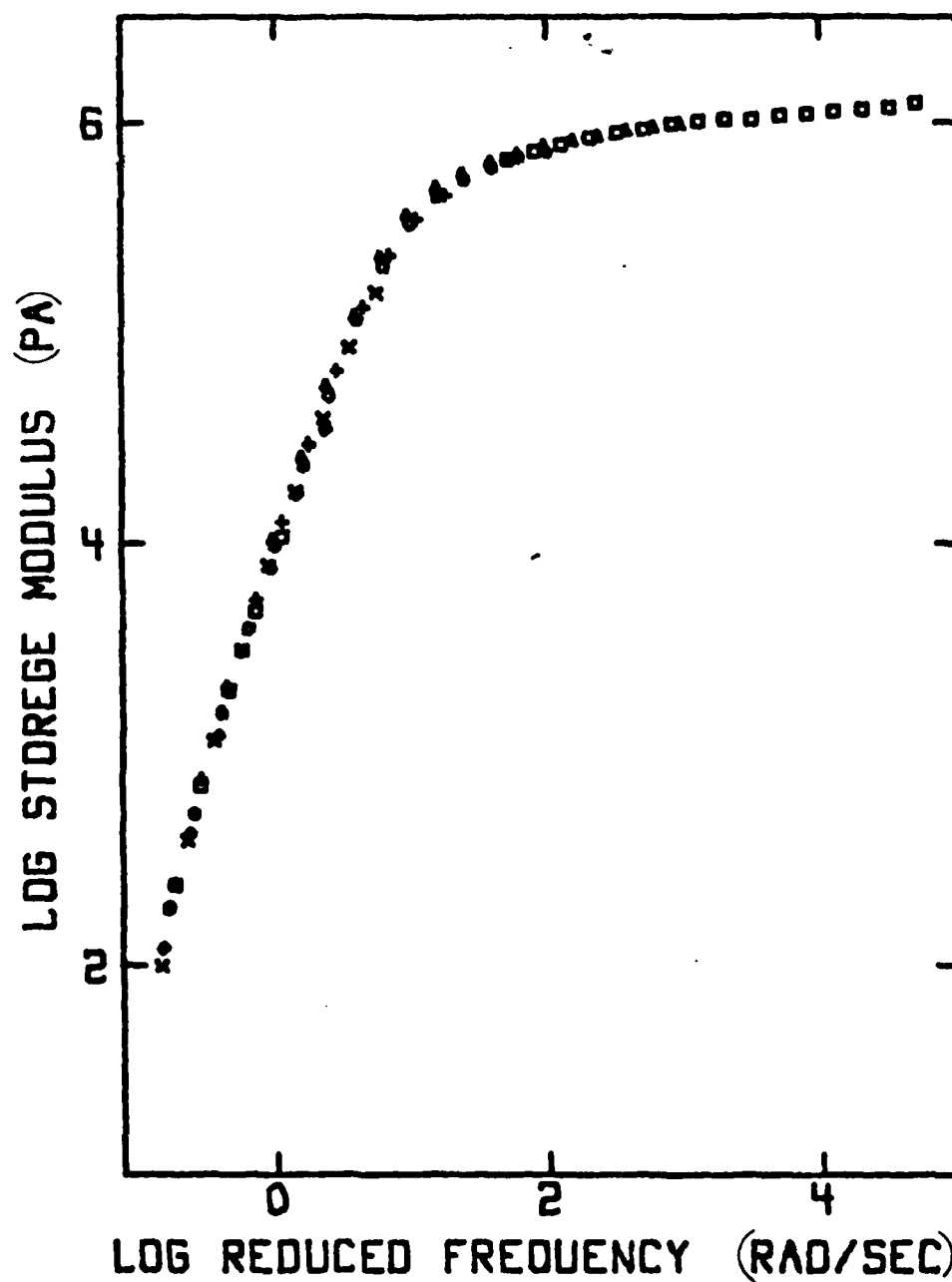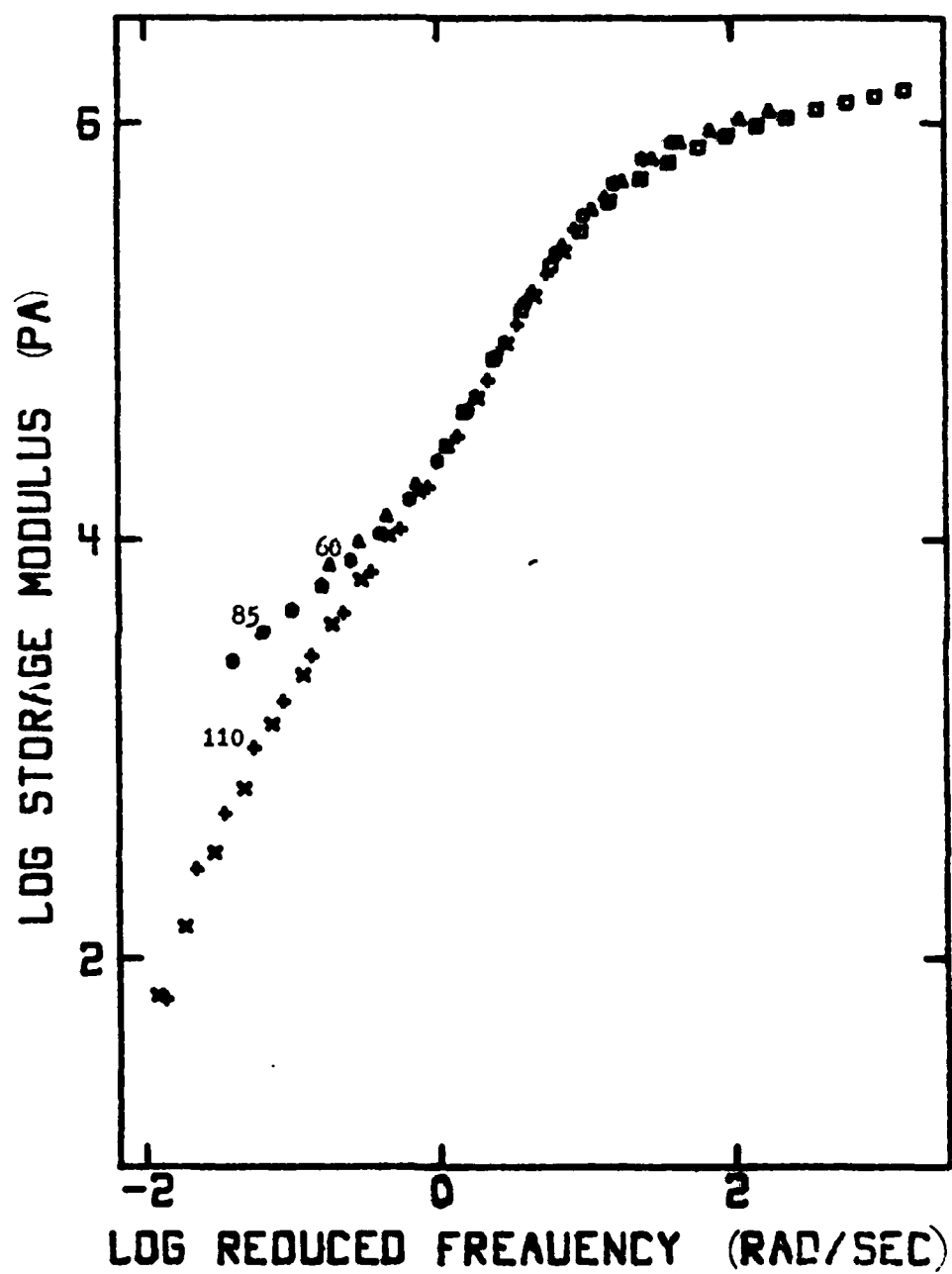
Figure 7. 90/0 G'_p master curve, with reference temperature at 70 °C.

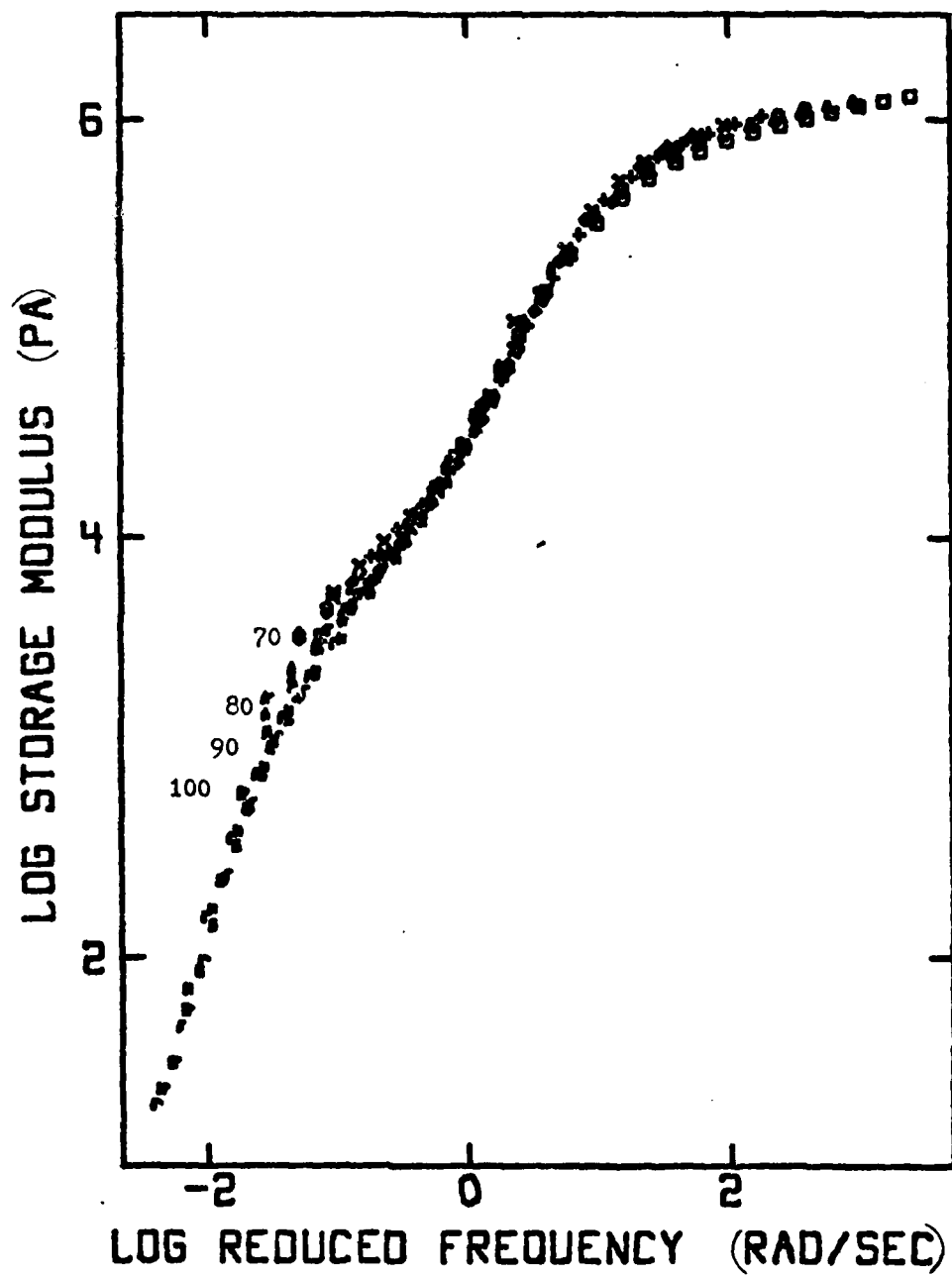Figure 8.   30/50A G'_p master curve; $T_{ref} = 70^o$ C.

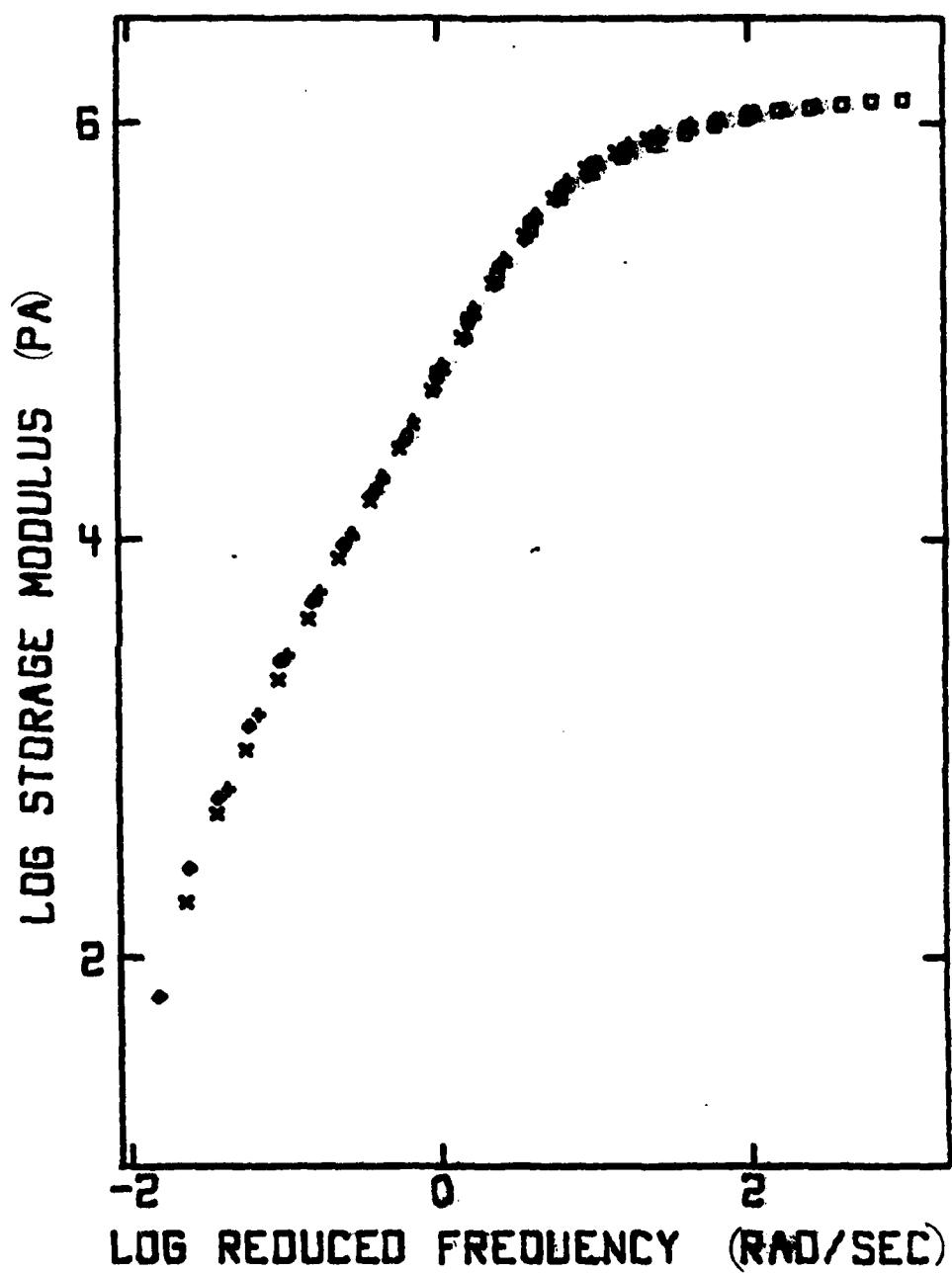Figure 9. 30/50B G'_p master curve, T_{ref} = 70° C.

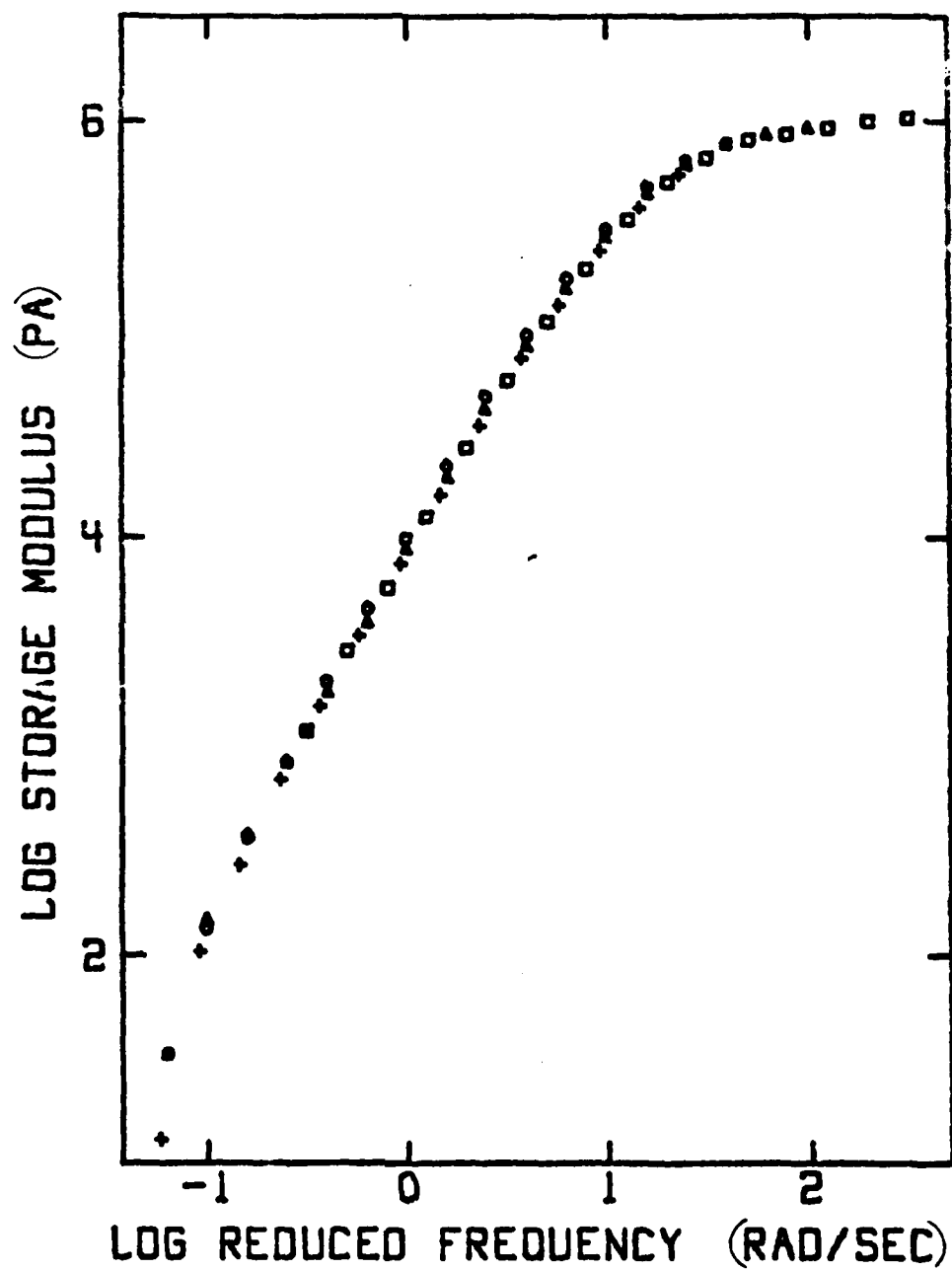Figure 10. 30/100 G_p' master curve, $T_{ref} = 70°$ C.

Figure 11.   0/100 C_p' master curve, reference temp. = 70°C.

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